Sorption and Transport of Pharmaceutical chemicals in Organic- and Mineral-rich Soils

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ABSTRACT. Pharmaceutical, active ingredients in personal care products (PhACs), and their derivative compounds are increasingly ubiquitous in surface waters across the world. Sorption and transport of four relatively common PhACs (naproxen, ibuprofen, cetirizine, and triclosan) in different natural soils was measured. All of these compounds are relatively hydrophobic (log $K_{OW}>2$) and have acid/base functional groups, including one compound that is zwitterionic (cetirizine.) The main goal of this study was to correlate organic matter (OM) and clay content in natural soils and sediment with sorption and degradation of PhACs and ultimately their potential for transport within the subsurface environment. A- and B-horizon soils were collected from four sub-regions within a pristine managed forested watershed near Charleston, SC, with no apparent sources of anthropogenic contamination. These four soil series had varying OM content (f_{OC}) between 0.4-9%, clay mineral content between 6-20%, and soil pH between 4.5-6. The A-horizon soils had higher f_{OC} and lower clay content than the B-horizon soils. Sorption isotherms measured from batch sorption experimental data indicated a non-linear sorption relationship in all A- and B-horizon soils – stronger sorption was observed at lower PhAC concentrations and lower sorption at higher concentrations. Three PhACs (naproxen, ibuprofen, and triclosan) sorbed more strongly with higher f_{OC} A-horizon soils compared with the B-horizon soils. These results show that soil OM had a significant role in strongly binding these three PhACs, which had the highest KOW values. In contrast, cetirizine, which is predominantly positively charged at pH below 8, strongly sorbed to soils with higher clay mineral content and least strongly to higher f_{OC} soils. All sorption isotherms fitted well to the Freundlich model. For naproxen, ibuprofen, and triclosan, there was a strong and positive linear correlation between the Freundlich adsorption constant, K_d, and f_{OC}, again indicating that these PhACs preferentially partition into soil OM. Such a correlation was absent for cetirizine. Breakthrough curves of PhACs measured in homogeneous packed soil columns indicated that PhAC transport was affected by chemical nonequilibrium processes depending on the soil and PhAC chemistry. The shape of the breakthrough curves indicated that there were two distinct sorption sites – OM and clay minerals – which influence nonequilibrium transport of these compounds. The retardation factor estimated using the distribution coefficient, K_d, measured from the sorption experiments was very similar to the measured value. While the sorption and transport data do not provide mechanistic information regarding the nature of PhAC interaction with chemical reactive components within geological materials, they do provide important information regarding potential fate of such compounds in the environment. The results also show the role that soil OM and mineral surfaces play in sequestering or transporting these chemicals. These insights have implications to the quality of the water resources in our communities.

INTRODUCTION

Pharmaceutical and active ingredients in personal care products (PhACs) are some of the most ubiquitous compounds found in surface water across the world. Recently, an investigation conducted by AP (http://hosted.ap.org/specials/interactives/pharmawater_site/index.html) determined that trace levels of a wide spectrum of PhACs were found in drinking water used by several million people across two dozen metropolitan areas across the US. Other surveys led by the US Geological Survey have determined that common medications such as ibuprofen, naproxen, cetirizine, etc. were some of the compounds detected in natural surface waters. These compounds could potentially cause endocrine-disruption in mammals and aquatic life. Because of their complex organic nature (some are nonpolar, others have multiple reactive moieties), these compounds are not very soluble in water and, hence, tend to accumulate in soils, sediments, and very importantly, in tissues of aquatic organisms. The most critical components that influence how strongly PhACs

accumulate in natural materials are the soil organic matter, clay mineral content, as well as soil pH. The main goal of this study is to quantify how strongly PhACs absorb onto soils and which soil properties influence the fate of these chemicals in natural systems. The main goal of this series of studies is to simulate groundwater transport of these PhACs in soils and ultimately determine if groundwater resources are susceptible to contamination or if soils and sediments on the surface can provide adequate protection to water resources. Another goal is to mathematically model these processes and forecast likelihood of contamination. Results from these studies could likely interest water treatment managers as well as researchers investigating impacts of anthropogenic chemicals on ecosystems.

PROJECT OBJECTIVES

The primary goal of this ongoing study is to determine whether organic compounds, such as ibuprofen and cetirizine, accumulate in soils and marsh sediments and, if they do, what geochemical controls affect how strongly they sorb onto these solid particles. Based on our previous studies, we hypothesized that nonpolar compounds, such as ibuprofen, naproxen, and triclosan, will display strong retardation behavior in soils that are enriched in organic-rich soils. We also hypothesized that zwitterionic compounds, such as cetirizine, will display strong retardation in soils enriched in clay minerals.

BACKGROUND AND RELATED WORK

The release of pharmaceutically active compounds (PhACs) into the environment is a problem of global concern. While the measured concentrations of these compounds in natural waters are well below medical dosage levels, studies of the risk to the ecosystem have indicated adverse effects to both aquatic and non-aquatic organisms (Daughton and Ternes, 1999; Halling-Sorenson et al., 1998). The risk posed by this mixture of PhACs to children, women of child-bearing age and people with compromised immune systems is not known. Several studies suggest that trace levels of these compounds have detrimental effect on endocrine functions in mammals and fish (Daughton and Ternes, 1999; Sumpter and Johnson, 2005). Other studies have indicated that these compounds persist in the environment for a long time either in their original form or as derivatives of original compounds (Daughton and Ternes, 1999; Snyder et al., 2003).

Pharmaceuticals enter natural water systems after passing through wastewater treatment plants that have proven to be relatively inefficient at removing many of these compounds (Snyder et al., 2003; Ternes et al.,

2004). A 2002 USGS study found that 80% of 139 streams across 30 states contained detectable levels of PhACs (Kolpin et al., 2002). Because of their continuous use and release from wastewater treatment plans, these compounds are considered to be pseudo-persistent (Daughton and Ternes, 1999).

To date, most of the research in this area has focused largely on the environmental occurrence of PhACs (Brooks et al., 2009). However, the environmental fate of PhACs is largely unknown. Once they enter the environment the main removal processes are microbial biodegradation, solar photodegradation, and sorption to soils and sediments. Pharmaceutical compounds are generally designed to resist biodegradation, so this route of removal is often negligible (Daughton and Ternes, 1999; Halling-Sorenson et al., 1998). One of the predominant processes that determines the environmental fate of PhACs is sorption to soils and sediments. Binding of several PhACs to a variety of soils have been reported, but actual transport characteristics of the compounds have not been reported so far (Matamoros and Bayona, 2006; Thiele-Bruhn, 2003; Tolls, 2001). Of the factors that have been reported to influence binding of PhACs to soils, the soil texture and the presence of soil organic matter (SOM) were deemed to be most critical. In addition, factors such as exchange capacity of soils and soil solution pH are also likely important for binding (Schwarzenbach et al., 2003). In soils that have high amounts of mineral and organic matter content it is, therefore, expected that the compounds are strongly retained.

METHODS

Sorption and column studies were performed on clean soils collected from Francis Marion National Forest, a relatively pristine forested watershed, as per previously developed techniques (Vulava et al., 2000; Vulava et al., 2002). A- and B-horizon soils were collected from four sub-regions where there were no apparent sources of anthropogenic contamination. These four soil series had varying OM content between 0.4-9% (f_{OC} = 0.004-0.9), clay mineral content between 6-20%, and soil pH between 4.5-6. The A-horizon soils had higher f_{OC} and lower clay content than the B-horizon soils. Sorption studies were conducted by spiking PhACs (naproxen, ibuprofen, triclosan and cetirizine) in these soils with varying OM content, clay mineral content, and soil pH. Spiked soil-water suspensions were monitored for changes in sorbate concentrations. Once equilibrium was attained, the suspensions were centrifuged, followed by analysis of the supernatant solution filtrate for PhAC concentrations. Once equilibrium concentrations were determined, sorption isotherms were plotted to determine

sorption capacity of the compounds and also K_d values (Vulava et al., 2000).

The K_d values were used to model transport of PhACs in soil environments using equilibrium advective-dispersive reactive transport equations (Toride et al., 1995). Different reactive transport scenarios that incorporate various sorption mechanisms were modeled. Chromatographic column experiments were also performed to simulate transport of PhACs in soil and groundwater environments (Vulava et al., 2002). The resulting breakthrough curves were compared with those from the model predictions for best fit of the data. These set of experiments helped determine the most important processes that influence the fate of PhACs in groundwater environments.

RESULTS AND DISCUSSION

Sorption of four PhACs (naproxen, ibuprofen, triclosan and cetirizine) in natural soils with varying soil chemistry was determined. The sorption isotherms (plot of PhAC in solution, c_i mg/L vs. PhAC sorbed, q_i mg/kg) indicated a non-linear relationship in all A- and B-horizon soils; stronger sorption was observed at lower PhAC concentrations and lower sorption at higher concentrations (Figure 1). That is, the distribution coefficient, K_d ($= q_i/c_i$) decreased with increasing concentration. Also, for each soil series, stronger sorption was observed for A-horizon soils compared to that with B-horizon soils, indicating that f_{OC} played a significant role in strongly binding PhACs. The exception to this observation was the opposite trend for cetirizine. Cetirizine preferentially sorbed with clay-rich (B-horizon) soils and only minimally with A-horizon soils. All sorption isotherms fit to Freundlich model ($q_i = K_f c_i^n$, where K_f and n are fitting parameters.) In general, the Freundlich distribution coefficient K_f was higher in A-horizon soils and $n<1$.

There was also a strong linear correlation between K_f and f_{OC}, indicating that each PhACs investigated preferentially partitioned into the SOM. During these investigations, it was assumed that PhACs do not degrade into other compounds during sorption experiments, but this may not be accurate as different fractions in the organic matter can potentially degrade these PhACs. Analysis of the aqueous suspensions as well as extracted soil samples for degradation compounds will be pursued in future studies. We also did not investigate the specific role clay mineral- and mineral oxide-surfaces play in sorption of ionized PhACs – many PhACs are ionized at environmentally relevant pH levels depending on their ionizable functional groups. Both naproxen and ibuprofen would be deprotonated (anionic) at these soil pH levels, while the majority of triclosan

species would be neutral; the presence of charged moieties on the PhAC would greatly influence sorption onto these mineral surfaces.

Preliminary transport experiments indicate that triclosan was significantly retarded in OM-rich A-horizon soil (Figure 2). The shape of the triclosan breakthrough curve in A-horizon soil also indicated presence of multiple reactive sorption surfaces of importance in these soils – likely OM, mineral (Fe, Al, Mn, etc.) oxide, and clay mineral surfaces.
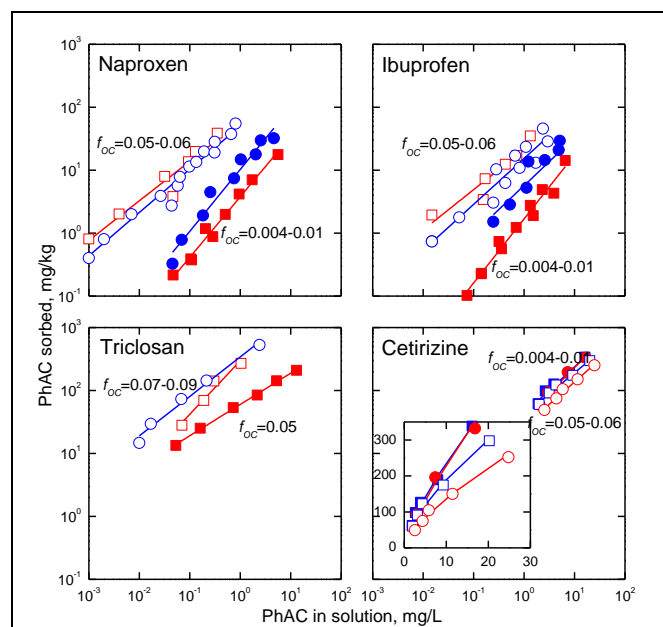

Figure 1. Sorption isotherms of four PhACs in OM-rich (open symbols) and clay material-rich (closed symbols) soils. Similar symbols are used for same soils with different OM content (denoted by f_{OC} values.) The lines indicate model fit of sorption isotherms to Freundlich non-linear model.
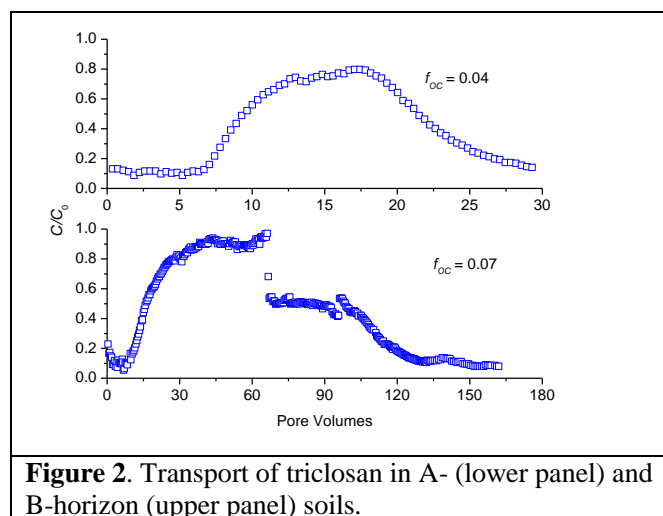

Figure 2. Transport of triclosan in A- (lower panel) and B-horizon (upper panel) soils.

While the sorption and transport data do not provide mechanistic information regarding the nature of PhAC interaction with chemical reactive components within geological materials, they do provide important information regarding potential fate of such compounds in the environment. The results also show the role that soil OM and mineral surfaces play in sequestering or transporting these chemicals. We continue to investigate various mechanisms by which PhACs degrade and transform in the environment. This understanding is ultimately critical in predicting how our ecosystems adapt to the presence of these new classes of anthropogenic contaminants. These insights have implications to the quality of the water resources in our communities.

ACKNOWLEDGEMENTS

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